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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C10L 1/18</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/17160</b> <b>(43) International Publication Date:</b> 4 August 1994 (04.08.94)
<b>(21) International Application Number:</b> PCT/EP94/00148 <b>(22) International Filing Date:</b> 20 January 1994 (20.01.94)  <b>(30) Priority Data:</b> 93011195 21 January 1993 (21.01.93) GB  <b>(71) Applicant (for all designated States except US):</b> EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CAPROTTI, Rinaldo [IT/GB]; White Witch House, East Hanney, Oxford- shire OX12 0HQ (GB). BOVINGTON, Charles, Herbert [GB/GB]; Asbourne, Kings Lane, Longcot, Faringdon, Oxfordshire SN7 7SS (GB). MACRAE, Colin, John, Dou- glas [GB/GB]; 8 Queens Road, Chandlers Ford, Eastleigh, Hampshire SO5 1AH (GB).  <b>(74) Agents:</b> MANSELL, Keith, Rodney et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).		<b>(81) Designated States:</b> AU, BR, CA, FI, JP, KR, NO, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FUEL COMPOSITION  <b>(57) Abstract</b>  A fuel oil composition comprises a major proportion of a liquid hydrocarbon middle distillate fuel having a sulphur concentration of 0.2 % or less by weight based on the weight of the fuel, and a minor proportion of a wear-reducing additive comprising an ester for increasing the lubricity of the fuel.		

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## Fuel Composition

This invention relates to fuel compositions useful, for example, to improve lubricity and reduce wear in diesel engines.

5 The art describes esters as additives for diesel engine fuel. For example, US-A-2,527,889 describes polyhydroxy alcohol esters as primary anti-corrosion additives in diesel engine fuel, and GB-A-1,505,302 describes ester combinations including, for example, glycerol monoesters and glycerol diesters as diesel fuel  
10 additives, the combinations being described as leading to advantages including less wear of the fuel-injection equipment, piston rings and cylinder liners.

GB-A-1,505,302 is, however, concerned with overcoming the operational disadvantages of corrosion and wear by acidic combustion products, residues in  
15 the combustion chamber and in the exhaust system. The document states that these disadvantages are due to incomplete combustion under certain operating conditions. Typical diesel fuels available at the date of the document contained, for example, from 0.5 to 1% by weight of sulphur, as elemental sulphur, based on the weight of the fuel.

20 The sulphur content of diesel fuels has now been or will be lowered in a number of countries for environmental reasons, i.e. to reduce sulphur dioxide emissions. Thus, heating oil and diesel fuel sulphur content are being harmonised by the CEC at a maximum of 0.2% by weight, and, at a second stage, the maximum  
25 content in diesel fuel will be 0.05% by weight. Complete conversion to the 0.05% maximum may be required during 1996.

The process for preparing low sulphur content fuels, in addition to reducing sulphur content, also reduces the content of other components of the fuel such as  
30 polyaromatic components and polar components. Reducing one or more of the sulphur, polyaromatic and polar component content of the fuel creates a new problem in use of the fuel, i.e. the ability of the fuel to lubricate the injection system of the engine is reduced such that, for example, the fuel injection pump of the engine can fail relatively early in the life of an engine, failure being, eg. in high  
35 pressure fuel injection systems such as high pressure rotary distributors, in-line pumps and unit injectors and injectors. Such severe failures are due to wear that

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is completely different from the corrosive wear problem described in GB-A-1,505,302.

5 As stated, such failure can occur early in the life of an engine; in contrast, the wear problems referred to in GB-A-1,505,302 occur late in the life of an engine. The problem created by adopting low sulphur content diesel fuels is described in, for example D. Wei and H. Spikes, Wear, Vol. 111, No. 2, p. 217, 1986; and R. Caprotti, C. Bovington, W. Fowler and M. Taylor SAE paper 922183; SAE fuels and lubes. meeting Oct. 1992; San Francisco, USA.

10 It has now been found that the above-mentioned wear problem due to use of fuels having a low sulphur content can be lessened or met by providing certain additives in the fuel.

15 Thus, a first aspect of the invention is a fuel oil composition comprising a major proportion of a liquid hydrocarbon middle distillate fuel oil having a sulphur concentration of 0.2% by weight or less, and a minor proportion of an additive comprising an ester of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has one or more carbon atoms.

20 A second aspect of the invention is the use of a fuel oil composition as defined in the first aspect of the invention as the fuel in a compression-ignition (diesel) engine for controlling wear rate in the injection system of the engine in operation of the engine.

25 A third aspect of the invention is a method of operating a compression-ignition (diesel) engine comprising providing a fuel oil composition as defined in the first aspect of the invention as the fuel in the engine thereby to control wear rate in the injection system of the engine.

30 The examples of this specification will demonstrate the efficacy of the additives of the invention in reducing wear when fuel oils of the invention are used.

35 Whilst not wishing to be bound by any theory, it is believed that of the additive, in use of the composition in a compression-ignition internal combustion engine, is capable of forming over the range of operating conditions of the engine, at least partial mono- or multi-molecular layers of the additive on surfaces of the injection

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system, particularly the injector pump that are in moving contact with one another, the composition being such as to give rise, when compared with a composition lacking the additive, to one or more of a reduction in wear, a reduction in friction, or an increase in electrical contact resistance in any test where two or more loaded bodies are in relative motion under non-hydrodynamic lubricating conditions.

The features of the invention will now be described in further detail.

## 10 ADDITIVE

As stated, it is believed that the additive, which may be a single additive or mixture of additives, is capable of forming at least partial layers on certain surfaces of the engine. By this is meant that the layer formed is not necessarily complete on the contacting surface. Thus, it may cover only part of the area of that contacting surface, for example 10% or more, or 50% or more. The formation of such layers and the extent of their coverage of a contacting surface can be demonstrated by, for example, measuring electrical contact resistance or electrical capacitance.

Examples of tests that can be used to demonstrate one or more of a reduction in wear, a reduction in friction or an increase in electrical contact resistance according to this invention are the Ball On Cylinder Lubricant Evaluator and High Frequency Reciprocating Rig tests which will be referred to hereinafter.

The acid, alcohol and ester will now be discussed in further detail as follows.

### (i) Acid

The acid from which the ester is derived may be a mono or polycarboxylic acid such as aliphatic, saturated or unsaturated, straight or branched chain, mono and dicarboxylic acids being preferred. For example, the acid may be generalised in the formula



where x represents an integer and is 1 or more such as 1 to 4, and R' represents a hydrocarbyl group having from 2 to 50 carbon atoms and which is mono or polyvalent corresponding to the value of x, the -COOH groups, when more than one is present, optionally being substituent on different carbon atoms from one another.

'Hydrocarbyl' means a group containing carbon and hydrogen which group is connected to the rest of the molecule via a carbon atom. It may be straight or branched chain which chain may be interrupted by one or more hetero atoms such as O, S, N or P, may be saturated or unsaturated, may be aliphatic or alicyclic or aromatic including heterocyclic, or may be substituted or unsubstituted. Preferably, when the acid is monocarboxylic, the hydrocarbyl group is an alkyl group or an alkenyl group having 10 (e.g. 12) to 30 carbon atoms, i.e. the acid is saturated or unsaturated. The alkenyl group may have one or more double bonds, such as 1, 2 or 3. Examples of saturated carboxylic acids are those with 10 to 22 carbon atoms such as capric, lauric, myristic, palmitic, and behenic acids and examples of unsaturated carboxylic acids are those with 10 to 22 carbon atoms such as oleic, elaidic, palmitoleic, petroselic, riconoleic, eleostearic, linoleic, linolenic, eicosanoic, galoleic, erucic and hypogeic acids. When the acid is polycarboxylic, having for example from 2 to 4 carboxy groups, the hydrocarbyl group is preferably a substituted or unsubstituted polymethylene.

(ii) Alcohol

The alcohol from which the ester is derived may be a mono or polyhydroxy alcohol such as a trihydroxy alcohol. For example, the alcohol may be generalised in the formula



where y represents an integer and is 1 or more and R<sup>2</sup> represents a hydrocarbyl group having 1 or more carbon atoms such as up to 10 carbon atoms, and which is mono or polyvalent corresponding to the value of y, the -OH groups, when more than one is present, optionally being substituent on different carbon atoms from one another.

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5 'Hydrocarbyl' has the same meaning as given above for the acid. For the alcohol, the hydrocarbyl group is preferably an alkyl group or a substituted or unsubstituted polymethylene group. Examples of monohydric alcohols are lower alkyl alcohols having from 1 to 6 carbon atoms such as methyl, ethyl, propyl and butyl alcohols.

10 Examples of polyhydric alcohols are aliphatic, saturated or unsaturated, straight chain or branched alcohols having 2 to 10, preferably 2 to 6, more preferably 2 to 4, hydroxy groups, and having 2 to 90, preferably 2 to 30, more preferably 2 to 12, most preferably 2 to 5, carbon atoms in the molecule. As more particular examples the polyhydric alcohol may be a glycol or diol, or a trihydric alcohol such as glycerol.

15 (iii) The Esters

The esters may be used alone or as mixtures of one or more esters and may be composed only of carbon, hydrogen and oxygen. Preferably the ester has a molecular weight of 200 or greater, or has at least 10 carbon atoms, or has both.

20 Examples of esters that may be used are lower alkyl esters, such as methyl esters, of the above exemplified saturated or unsaturated monocarboxylic acids. Such esters may, for example, be obtained by saponification and esterification of natural fats and oils of plant or animal origin or by their transesterification with lower aliphatic alcohols.

25 Examples of esters of polyhydric alcohols that may be used are those where all of the hydroxy groups are esterified, those where not all of the hydroxy groups are esterified, and mixtures thereof. Specific examples are esters prepared from trihydric alcohols and one or more of the above-mentioned saturated or unsaturated carboxylic acids, such as glycerol monoesters and glycerol diesters, e.g. glycerol monooleate, glycerol dioleate and glycerol monostearate. Such polyhydric esters may be prepared by esterification as described in the art and/or may be commercially available.

35 The ester may have one or more free hydroxy groups.

## FUEL OIL

Preferably, the sulphur concentration is 0.05% by weight or less, such as 0.01%  
5 by weight or less, and may be as low as 0.005% by weight, or 0.0001% by weight, or lower. The art describes methods for reducing the sulphur concentration of hydrocarbon distillate fuels, such methods including for example solvent extraction, sulphuric acid treatment, and hydrodesulphurisation.

10 By "tricyclic aromatic" is meant a fixed system where three aromatic rings are fused together. Preferably, the fuel contains less than 1% by weight of such a component.

Examples of "polar components" are compounds such as those containing O, S  
15 or N; and esters; and alcohols.

The above-mentioned wear problem is found to become progressively more acute as the polar component concentration of the fuel is decreased; for  
example, it may be particularly severe at concentrations below 250 ppm, such as  
20 below 200 ppm and specifically in fuels having polar component concentrations of 170 ppm and 130 ppm respectively. Such polar component concentrations may conveniently be measured by High Pressure Liquid Chromatography, sometimes referred to as HPLC.

25 Middle distillate fuel oils to which this invention is applicable generally boil within the range of about 100°C to about 500°C, e.g. about 150°C to about 400°C. The fuel oil can comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillates are kerosene, jet  
30 fuels, diesel fuels, heating oils and heavy fuel oils, diesel fuels being preferred in the practice of the present invention for the above-mentioned reasons. The heating oil may be a straight atmospheric distillate, or it may contain amounts, e.g. up to 35% by weight of vacuum gas oil or of cracked gas oils or of both.

35 The concentration of the additive of the invention in the fuel oil may be up to 250,000 ppm, for example up to 10,000 ppm such as 1 to below 1000 ppm



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(active ingredient) by weight per weight of fuel, preferably 10 to 500 ppm, more preferably 10 to 200 ppm.

- The additive may be incorporated into bulk fuel oil by methods known in the art.
- 5 Conveniently, the additive may be so incorporated in the form of a concentrate comprising an admixture of the additive and a liquid carrier medium compatible with the fuel oil, the additive being dispersed in the liquid medium. Such concentrates preferably contain from 3 to 75 wt%, more preferably 3 to 60 wt%, most preferably 10 to 50 wt% of the additive, preferably in solution in the oil.
- 10 Examples of carrier liquid are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene and heater oil; aromatic hydrocarbons; paraffinic hydrocarbons such as hexane and pentane; and alkoxyalkanols such as 2-butoxyethanol. The carrier liquid must of course be selected having regard to its compatibility with the additive and with the fuel.

15

## CO-ADDITIVES

- The additives of the invention may be used singly or as mixtures of more than one additive. They may also be used in combination with one or more co-
- 20 additives such as known in the art, for example the following: detergents, antioxidants (to avoid fuel degradation), corrosion inhibitors, dehazers, demulsifiers, metal deactivators, antifoaming agents, cetane improvers, cosolvents, package compatibilisers, and middle distillate cold flow improvers.

## 25 EXAMPLES

The following examples illustrate the invention. The following materials and procedures were used and the results were as follows.

### 30 Additives

D: Glycerol monooleate.

E: Di-isodecyl adipate.

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Fuels

The fuels used, designated I and II, were diesel fuels having the following characteristics

5	I	S content	<0.01% (wt/wt)
		Aromatics content	<1% (wt/wt)
		Cetane number	55.2 to 56.1
		Cold Filter Plugging Point Temperature (CFPPT)	-36°C
10		95% boiling point	273°C
	II	S content	<0.01% (wt/wt)
		Aromatics	not measured
		Cetane number	not measured
15		CFPPT	-41°C
		95% boiling point	263°C

Tests

- 20 Certain of Additives D and E were dissolved in certain of fuels I and II and the resulting composition tested using:
- o the Ball On Cylinder Lubricant Evaluator (or BOCLE) test described in Friction and wear devices, 2nd Ed., p. 280, American Society of Lubrication Engineers, Park Ridge Ill. USA; and F. Tao and J. Appledorn, ASLE trans., 11, 345-352 (1968); and
  - o the High Frequency Reciprocating Rig (or HFRR) test described in D. Wei and H. Spikes, Wear, Vol. 111, No. 2, p. 217, 1986; and R. Caprotti, C. Bovington, W. Fowler and M. Taylor SAE paper 922183; SAE fuels and lubes. meeting Oct. 1992; San Francisco, USA.

Both tests are known to provide a measure of the lubricity of a fuel.

Results

The tables below give the results.

5 (A) BOCLE Test

The results are given as the wear scar diameter. A lower value therefore indicates less wear than a higher value. All tests were done at ambient temperature.

10

Fuel I

Additive	Additive Concentration (ppm; wt/wt)	Result ( $\mu\text{m}$ )
Base Fuel	-	852
D	200	505

Fuel II

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Additive	Additive Concentration (wt%)	Result ( $\mu\text{m}$ )
Base Fuel	-	700
D	50	570
D	100	500
D	200	520
D	500	480
D	1,000	430

(B) HFRR Test

The results are also expressed as wear scar diameter. Additionally, coefficient of friction was measured. Tests were done at different temperatures as indicated. In Fuel I, Additive D's concentration was 200 ppm (wt/wt) and Additive E's concentration was 10,000 ppm. In Fuel II, Additive D's concentration is indicated in parentheses.

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Fuel I

	20°C		25°C	60°C	
Additive	Coefficient of Friction	Wear Scar Diameter (µm)	Wear Scar Diameter (µm)	Coefficient of Friction	Wear Scar Diameter (µm)
Base	0.59	540	576	0.72	590
D	0.19	240	180	0.19	160
E			344		442

Fuel II

	20°C		60°C	
Additive	Coefficient of Friction	Wear Scar Diameter (µm)	Coefficient of Friction	Wear Scar Diameter (µm)
Base Fuel	0.60	600	0.75	630
D (10 ppm)	0.95	530	0.83	570
D (50 ppm)	0.55	580	0.58	590
D (100 ppm)	0.41	530	0.39	560
D (150 ppm)	0.21	0	0.22	240
D (200 ppm)	0.23	<20	0.23	250
D (1000 ppm)	0.22	0	0.23	250

5

The results show that lubricity is improved by using additives D and E.

Claims:

1. A fuel oil composition comprising a major proportion of a liquid hydrocarbon middle distillate fuel oil having a sulphur concentration of 0.2% by weight or less, and a minor proportion of an additive comprising an ester of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has one or more carbon atoms.
2. The composition of claims 1 wherein the sulphur concentration is 0.05% by weight or less.
3. The composition of claim 2 wherein the sulphur concentration is 0.01% by weight or less.
4. The composition of any of the preceding claims wherein the acid from which the ester is derived has the general formula
$$R'(COOH)_x$$
where x represents an integer from 1 to 4 and R' represents a hydrocarbyl group.
5. The composition of claim 4 wherein the acid is a monocarboxylic acid having 10 to 30 carbon atoms, which acid is saturated or is unsaturated by having 1 to 3 double bonds in an alkenyl group.
6. The composition of claim 5 wherein the acid has 12 to 22 carbon atoms.
7. The composition of claim 4 wherein the acid is a polycarboxylic acid having from 2 to 4 carboxy groups and R' is a substituted or unsubstituted polymethylene group.
8. The composition of claim 7 wherein the acid is a dicarboxylic acid.
9. The composition of any of the preceding claims wherein the alcohol is an alkyl alcohol having from 1 to 6 carbon atoms.

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10. The composition of claim 9 wherein the alcohol is methanol.
11. The composition of any of claims 1 to 8 wherein the alcohol is an aliphatic, saturated or unsaturated, straight chain or branched polyhydric alcohol having 2 to 10 hydroxy groups and 2 to 90 carbon atoms in the molecule.
12. The composition of claim 11 wherein the alcohol has 2 to 4 hydroxy groups and 2 to 5 carbon atoms in the molecule.
13. The composition of claim 12 wherein the alcohol is glycerol.
14. The composition of claim 13 wherein the ester is glycerol monooleate.
15. The composition of any of the preceding claims wherein the concentration of additive in the fuel oil is in the range of 10 to 10,000 ppm by weight of active ingredient per weight of fuel oil.
16. The composition of claim 15 wherein the concentration is 100 to 200 ppm.
17. The use of a fuel oil composition of any of the preceding claims as the fuel in a compression-ignition engine for controlling wear rate in the injection system of the engine in operation of the engine.
18. A method of operating a compression-ignition engine comprising providing a fuel oil composition of any of the preceding claims as the fuel in the engine thereby to control wear rate in the injection system of the engine.
19. The use of claim 17 or method of claim 18 wherein the wear is in the injection pump of the engine.

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## INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/EP 94/00148

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C10L1/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,1 405 551 (ESSO) 31 May 1965 see page 2 - page 3 ---	1-19
X	DE,A,15 94 417 (ESSO) 6 May 1970  see page 4 - page 5 ---	1-4,7-9, 11,12, 15-19
X	US,A,2 993 773 (STROMBERG) 25 July 1961  see column 15, line 50 -----	1,2,4, 7-12,15, 16



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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4 March 1994

Date of mailing of the international search report

31. 03. 94

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# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 94/00148

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-1405551		DE-A- 1594420 GB-A- 1065398 US-A- 3273981	23-07-70
DE-A-1594417	06-05-70	BE-A- 676874 FR-A- 1425100 GB-A- 1047493 NL-A- 6400328 NL-A- 6502554	22-08-66  26-10-64 03-09-65
US-A-2993773		NONE	